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Measurements of nonmethane hydrocarbons in 28 United States cities

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Abstract

Between 1999 and 2005 a sampling campaign was conducted to identify and quantify the major species of atmospheric nonmethane hydrocarbons (NMHCs) in United States cities. Whole air canister samples were collected in 28 cities and analyzed for methane, carbon monoxide (CO) and NMHCs. Ambient mixing ratios exhibited high inter- and intra-city variability, often having standard deviations in excess of 50% of the mean value. For this reason, ratios of individual NMHC to CO, a combustion tracer, were examined to facilitate comparison between cities. Ratios were taken from correlation plots between the species of interest and CO, and most NMHCs were found to have correlation coefficients (r^2) greater than 0.6, particularly ethene, ethyne and benzene, highlighting the influence of vehicular emissions on NMHC mixing ratios. Notable exceptions were the short-chain alkanes, which generally had poor correlations with CO. Ratios of NMHC vs. CO were also used to identify those cities with unique NMHC sources.

Keywords: NMHCs; Carbon monoxide; Vehicular emissions; Urban air pollution; Ozone precursors

1. Introduction

Nonmethane hydrocarbons (NMHCs), a class of volatile organic compounds (VOCs), are an important component of urban air pollution because of their role in the formation of tropospheric ozone (O_3) and, in the case of aromatic NMHCs, the formation of secondary organic aerosols (Derwent, 1995; Odum et al., 1997). Additionally, many species, such as benzene and *n*-hexane, are known to affect human health. NMHCs are emitted by both anthropogenic and biogenic sources, although in most urban environments the anthropogenic sources are dominant. Anthropogenic emissions are from both mobile sources, namely automobiles, and stationary sources, such as power plants and industrial complexes.

In the urban troposphere, transportation-related emissions normally constitute a large fraction of NMHC sources (Fujita et al., 1995; Colvile et al., 2001). Alkenes and alkynes are strongly associated

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with combustion processes and emissions from internal combustion engines, while C_5–C_8 alkanes are common components of vehicular fuels and are associated with the unburned portion of tailpipe emissions (Watson et al., 2001). These alkanes are also present in evaporated fuels from vehicles and fueling stations. Transportation-related sources of aromatic hydrocarbons include vehicular exhaust (where they are emitted as both combustion products and unburned fuel) and fuel evaporation. Some aromatic species, such as toluene, are used in industrial processes, which can make their transportation fraction relatively less significant. The lighter alkanes (C_2–C_4) are not strongly associated with vehicular emissions, but are found as components of other fuels such as natural gas and liquefied petroleum gas (LPG) (Harley et al., 1992; Blake and Rowland, 1995).

In polluted environments the photo-oxidation of NMHCs in the presence of nitrogen oxides ($NO_x = NO + NO_2$) leads to the formation of the secondary pollutant ozone (Calvert, 1976; Seinfeld, 1989; Finlayson-Pitts and Pitts, 2000). The detrimental health effects of ground-level ozone have led to its position as a primary target of air quality regulations, and tremendous effort has been put into controlling ground-level ozone formation. The initial step in the production of ozone is the reaction between a NMHC and the hydroxyl radical (OH). Therefore, the relative contributions of individual NMHC species to ozone formation vary based on each compound's rate of reaction with OH. These rates are well studied for the most abundant NMHCs (Atkinson, 2000) and predictions of ozone production can be made when mixing ratios of ozone precursors are known (e.g. Carter, 1994). Knowledge of a city's speciated NMHC composition and sources provides a better understanding of urban ozone formation potential, and can assist in the formulation of control strategies.

Here we present results from a study designed to identify and quantify the major NMHC species present in United States cities. Over a 6-year period, between August 1999 and August 2005, VOC measurements were made from whole air samples collected in 28 cities. These samples were collected during the daytime hours, between 10 am and 7 pm local time. All samples were analyzed for methane (CH_4), carbon monoxide (CO) and NMHCs.

In addition to ambient NMHC mixing ratios, ratios of NMHCs to CO are examined. While ambient mixing ratios are useful for understanding the magnitude of hydrocarbon pollution, these can vary widely within a city and between different cities as a result of a number of factors such as dilution and differences in source strengths, as well as local meteorology and geography. Normalizing to an urban tracer accounts for these factors and provides insight into relative mixing ratios, allowing for a more useful comparison of measurements from different locations and cities. Carbon monoxide, a product of incomplete combustion, is commonly used as a marker for vehicular emissions and is strongly associated with urban pollution (Fujita et al., 1992; Harley et al., 2001; Parrish, 2006). Therefore, examination of NMHC to CO ratios allow for the comparison of otherwise highly variable NMHC mixing ratios.

Relatively few speciated hydrocarbon studies have been conducted in multiple US cities (Sexton and Westberg, 1984; Edgerton et al., 1989; Seila et al., 1989; Evans et al., 1992; Mohamed et al., 2002). The most comprehensive study was carried out by the United States Environmental Protection Agency (EPA) from 1984 to 1986 in 39 different US cities (Seila et al., 1989). Samples in that study were collected during the morning hours (between 6 am and 9 am) and at one or two sites in each city. Speciation of NMHC was determined for 15% of those samples, selected because they were collected during periods of high ozone or had unusually high total NMHC.

2. Methods

Whole air canister samples were collected over a 5-week period every summer (August and the first week of September) in one to six United States cities between 1999 and 2005. These samples were collected as part of a seasonal urban study, in which one or two of the cities from the summertime sampling period were chosen for more intensive study in the following November, February and May (Doezema, 2004). Only the August/September measurements are examined in this work. Over 500 samples were collected in the 28 cities (Table 1). Three of these cities, New York, Philadelphia and Salt Lake City, were studied in two different years, for a total of 31 separate sampling campaigns.

In general, sampling locations were chosen to minimize the influence of point sources; selected sites were well-ventilated areas removed from roadsides, such as parks, schools and cemeteries. This allowed for the collection of well-mixed samples that were representative of a mixture of sources. The exceptions were for samples collected in New York

Table 1
Year of study and number of samples for the 28 cities that were studied

City	Year	Samples
Baltimore, MD	2000	18
Baton Rouge, LA	2001	18
Birmingham, AL	2001	17
Boston, MA	2003	22
Charleston, WV	2002	18
Charlotte, NC	2002	19
Chicago, IL	1999	16
Cleveland, OH	2004	17
Denver, CO	2004	13
Detroit, MI	2004	20
El Paso, TX	2003	19
Fresno, CA	2002	10
Houston, TX	1999	16
Knoxville, TN	2002	20
Las Vegas, NV	2000	10
Los Angeles, CA	2005	10
Milwaukee, WI	2001	14
New York City, NY[a]	1999	14
New York City, NY	2003	20
Oklahoma City, OK	1999	17
Philadelphia, PA[a]	2000	18
Philadelphia, PA	2004	20
Phoenix, AZ	2003	21
Pittsburgh, PA	2002	17
Providence, RI	2003	23
Richmond, VA	2004	18
Saint Louis, MO	2001	13
Salt Lake City, UT[a]	1999	17
Salt Lake City, UT	2004	19
San Diego, CA	2000	15
Washington, DC	2003	21

[a]Includes roadside/vehicular locations (see text).

City, Philadelphia and Salt Lake City in 1999 and 2000, which were obtained from both well-ventilated and roadside locations, with the latter selected to be representative of transportation-related emissions (noted in Table 1). During the 2nd of study for each of these cities (2003 for New York City and 2004 for Philadelphia and Salt Lake City) samples were collected in well-ventilated areas according to the standard protocol. For all cities in all years the majority of sampling locations were unique (i.e. not co-located), although at some locations multiple samples were collected at different times of day and on different days. Sampling times were restricted to between 10 am and 7 pm. local time to ensure consistent boundary layer height, and all samples were collected approximately 2 m above the ground.

Whole air samples were collected in 2 L electropolished, stainless steel sampling canisters fitted with a stainless steel bellows valve. The canisters were pre-treated and evacuated prior to use, and during sampling were filled to atmospheric pressure over approximately 1 min. After sample collection, the canisters were returned to our laboratory at the University of California, Irvine for analysis.

Detailed descriptions of our gas chromatographic (GC) systems are provided in Colman et al. (2001), Barletta et al. (2002) and Simpson et al. (2002) and only a brief description will be given here. Methane and CO were analyzed on species-specific GC systems. Methane analysis was performed using GC with a flame ionization detector (FID). CO was analyzed through separation using packed column GC, followed by catalytic conversion to CH_4 and subsequent detection by FID.

NMHCs were analyzed on a three GC system employing five column/detector combinations. An aliquot of the sample (1316 cm^3 at STP) was first preconcentrated on a glass bead-filled stainless steel loop immersed in liquid nitrogen. The loop was then heated using a hot water bath to volatize the sample. The volatized sample was then flushed by a helium carrier gas through the loop to a splitter that reproducibly (but not equally) split the sample into five aliquots that are output to the five column/detector combinations housed in three Hewlett-Packard (HP-6890) ovens. The first GC houses both a J&W Scientific DB-5ms column coupled with a quadrupole mass spectrometer detector (MSD) and a combination RESTEK-1701/DB-5 column coupled with an electron capture detector (ECD). A second GC houses a RESTEK-1701 column plumbed to an ECD and a combination J&W PLOT/J&W DB-1 column output to an FID. The third GC houses a J&W DB-1 connected to an FID.

For all three analytical systems, calibrated whole air standards were used for peak quantification, instrument calibration and to verify stable detector response. Here we report those NMHC species that were above our detection limit of 8 parts per trillion by volume (pptv) in the majority of samples and cities. The only exceptions are *n*-heptane, which was not measured in 1999 and *i*-butene, *m*-xylene and *p*-xylene, which were not measured during 1999 and 2000.

3. Results and discussion

3.1. Ambient mixing ratios

Mean mixing ratios for CH_4, CO and 21 NMHCs are given in Table 2. For cities studied in two

Table 2
Mean mixing ratios of CH_4, CO and 21 NMHCs in 28 cities (units are pptv unless otherwise stated)

City	CH_4 (ppmv)	CO (ppbv)	Ethane	Propane	*n*-Butane	*i*-Butane	*n*-Pentane	*i*-Pentane	*n*-Hexane	*n*-Heptane[a]	*n*-Octane
Baltimore	1.95 (0.09)	400 (64)	1660 (380)	1010 (300)	290 (110)	240 (58)	150 (47)	400 (110)	97 (36)	44 (17)	20 (10)
Baton Rouge	1.97 (0.04)	260 (52)	3150 (550)	1640 (350)	680 (250)	640 (240)	320 (56)	590 (100)	84 (21)	250 (63)	11 (3)
Birmingham	1.88 (0.04)	280 (84)	1090 (190)	580 (150)	280 (130)	120 (63)	160 (100)	460 (280)	110 (87)	78 (31)	16 (11)
Boston	1.88 (0.02)	230 (23)	1310 (210)	500 (98)	190 (53)	150 (52)	110 (31)	310 (92)	56 (16)	82 (25)	9 (3)
Charleston	1.91 (0.10)	160 (24)	8740 (2960)	3540 (1020)	1010 (350)	440 (170)	270 (110)	500 (220)	77 (32)	34 (13)	12 (6)
Charlotte	1.79 (0.01)	150 (22)	560 (71)	290 (110)	160 (57)	77 (34)	110 (40)	280 (120)	43 (17)	43 (16)	8 (6)
Chicago	1.89 (0.04)	410 (76)	1990 (500)	1010 (480)	470 (150)	260 (110)	420 (140)	1060 (330)	210 (73)		38 (12)
Cleveland	1.92 (0.06)	210 (36)	2630 (1470)	1330 (600)	620 (230)	270 (120)	280 (120)	560 (210)	82 (39)	38 (26)	12 (6)
Denver	1.80 (0.04)	200 (65)	1210 (440)	440 (200)	400 (190)	290 (140)	310 (150)	580 (290)	110 (60)	40 (21)	14 (7)
Detroit	1.98 (0.13)	380 (180)	3360 (1870)	1910 (1190)	1170 (910)	500 (310)	870 (730)	2170 (1940)	250 (150)	110 (69)	39 (24)
El Paso	1.83 (0.01)	180 (44)	3440 (860)	1920 (600)	580 (200)	260 (100)	230 (110)	400 (250)	84 (50)	47 (21)	13 (7)
Fresno	2.25 (0.32)	440 (110)	2500 (950)	2700 (2230)	650 (600)	780 (940)	400 (240)	910 (610)	140 (110)	88 (56)	23 (18)
Houston	1.77 (0.04)	230 (82)	1620 (800)	840 (530)	340 (200)	240 (150)	230 (120)	600 (320)	130 (63)		45 (18)
Knoxville	1.85 (0.04)	250 (48)	1050 (280)	740 (220)	570 (250)	180 (78)	300 (120)	800 (360)	84 (33)	39 (13)	12 (5)
Las Vegas	1.76 (0.01)	290 (130)	750 (140)	350 (110)	640 (480)	180 (120)	250 (190)	780 (620)	85 (56)	37 (18)	61 (32)
Los Angeles	1.95 (0.09)	560 (230)	6610 (2770)	6050 (3580)	2340 (1310)	1240 (600)	1200 (700)	2790 (1580)	390 (220)	160 (76)	80 (48)
Milwaukee	1.88 (0.03)	300 (68)	1920 (350)	1110 (450)	340 (95)	210 (80)	210 (120)	520 (280)	120 (54)	330 (70)	89 (60)
New York City (1999)	1.91 (0.10)	350 (120)	1630 (600)	760 (460)	510 (380)	720 (1110)	300 (200)	870 (620)	130 (85)		100 (75)
New York City (2003)	1.92 (0.07)	260 (72)	2070 (730)	870 (490)	420 (470)	320 (230)	180 (100)	400 (240)	180 (140)	48 (40)	260 (140)
Oklahoma City	1.81 (0.03)	270 (75)	4420 (1980)	3170 (1840)	1700 (940)	600 (310)	700 (410)	1220 (580)	260 (150)		94 (160)
Philadelphia (2000)	1.92 (0.09)	390 (200)	1580 (810)	1290 (1110)	450 (430)	360 (320)	270 (240)	600 (570)	130 (130)	62 (42)	44 (26)
Philadelphia (2004)	1.96 (0.11)	290 (100)	3340 (2360)	2080 (1270)	760 (580)	760 (620)	390 (250)	750 (430)	160 (95)	80 (44)	33 (22)
Phoenix	1.80 (0.01)	170 (37)	1050 (130)	620 (240)	200 (90)	82 (36)	220 (150)	440 (250)	62 (39)	38 (18)	9 (4)
Pittsburgh	2.09 (0.23)	220 (47)	7800 (4050)	2510 (1240)	720 (360)	470 (260)	310 (150)	460 (220)	93 (49)	55 (25)	14 (7)
Providence	1.91 (0.05)	250 (53)	1980 (250)	1050 (540)	300 (160)	180 (110)	170 (99)	380 (270)	69 (49)	59 (32)	18 (20)
Richmond	1.88 (0.07)	170 (43)	1400 (300)	590 (290)	160 (110)	100 (58)	110 (77)	240 (180)	40 (30)	24 (27)	16 (7)
Saint Louis	1.86 (0.03)	240 (43)	1590 (290)	1060 (490)	350 (140)	210 (130)	220 (91)	430 (160)	110 (37)		17 (4)
Salt Lake City (1999)	1.77 (0.02)	380 (210)	1070 (810)	600 (490)	720 (540)	290 (300)	620 (470)	1200 (930)	280 (230)		46 (29)
Salt Lake City (2004)	1.86 (0.05)	290 (130)	1840 (1930)	1730 (1840)	1340 (1120)	1260 (1890)	810 (480)	1340 (760)	240 (140)	100 (65)	34 (21)
San Diego	1.85 (0.07)	640 (270)	1900 (710)	1560 (960)	550 (290)	320 (200)	420 (250)	1210 (690)	170 (110)	67 (36)	65 (41)
Washington, D.C.	1.98 (0.14)	380 (150)	2190 (770)	1070 (640)	400 (270)	210 (160)	270 (200)	640 (480)	170 (160)	62 (49)	22 (23)

Table 2 (*continued*)

City	Ethene	Propene	1-Butene[c]	*i*-Butene[a,b]	Isoprene	Ethyne	Benzene	Toluene	Ethylbenzene	*o*-Xylene	*m*-Xylene[a]	*p*-Xylene[a]
Baltimore	750 (230)	190 (57)	32 (8)		510 (230)	890 (220)	190 (45)	1540 (880)	130 (49)	210 (85)	200 (43)	100 (43)
Baton Rouge	570 (210)	81 (47)	19 (13)	53 (240)	1160 (710)	520 (170)	150 (30)	540 (150)	20 (9)	18 (11)	27 (20)	19 (12)
Birmingham	540 (380)	130 (130)	22 (14)	69 (37)	1070 (720)	610 (360)	170 (100)	460 (300)	39 (35)	37 (35)	71 (73)	40 (44)
Boston	330 (31)	73 (31)	19 (6)	72 (31)	1000 (720)	420 (82)	93 (24)	220 (61)	21 (7)	18 (7)	29 (13)	16 (7)
Charleston	380 (150)	90 (33)	15 (6)	38 (15)	1820 (850)	300 (95)	84 (33)	120 (55)	21 (10)	20 (7)	32 (12)	16 (16)
Charlotte	320 (130)	78 (36)	14 (27)	49 (27)	1310 (570)	260 (84)	60 (24)	210 (75)	28 (14)	21 (10)	38 (22)	21 (10)
Chicago	1290 (460)	340 (120)	15 (5)		370 (340)	920 (260)	230 (60)	1430 (860)	180 (130)	260 (210)		
Cleveland	370 (170)	76 (38)	20 (10)	46 (17)	760 (480)	500 (210)	130 (41)	250 (140)	33 (20)	31 (20)	48 (38)	33 (26)
Denver	540 (350)	130 (92)	22 (13)	54 (33)	570 (330)	430 (310)	130 (67)	280 (180)	26 (17)	22 (12)	39 (26)	18 (11)
Detroit	1660 (1050)	430 (300)	76 (43)	110 (58)	170 (150)	1510 (950)	470 (270)	1190 (740)	160 (130)	170 (140)	280 (200)	150 (140)
El Paso	370 (250)	96 (65)	24 (13)	62 (18)	47 (75)	430 (250)	150 (71)	330 (200)	34 (27)	34 (32)	51 (50)	29 (27)
Fresno	860 (690)	170 (150)	39 (23)	120 (110)	710 (800)	1260 (650)	210 (86)	500 (390)	45 (34)	49 (44)	67 (54)	46 (46)
Houston	840 (680)	190 (92)	13 (11)		1240 (550)	500 (260)	160 (71)	660 (340)	110 (120)	210 (200)		
Knoxville	740 (370)	170 (99)	22 (8)	46 (21)	920 (1110)	690 (330)	140 (55)	300 (140)	79 (31)	58 (51)	88 (91)	44 (40)
Las Vegas	520 (400)	200 (120)	46 (19)		84 (79)	540 (420)	150 (76)	330 (190)	47 (39)	85 (72)	89 (87)	37 (30)
Los Angeles	2430 (1360)	490 (280)	65 (35)	130 (99)	270 (130)	2380 (1480)	480 (240)	1380 (720)	210 (140)	200 (130)	410 (290)	210 (170)
Milwaukee	560 (300)	140 (75)	27 (9)	74 (23)	120 (160)	630 (240)	180 (63)	630 (220)	33 (18)	32 (20)	59 (40)	31 (21)
New York City (1999)	1090 (550)	320 (160)	27 (24)		350 (430)	1050 (560)	210 (110)	1240 (760)	260 (250)	370 (370)		
New York City (2003)	750 (430)	250 (140)	41 (28)	120 (93)	740 (440)	640 (250)	190 (93)	880 (680)	370 (220)	260 (220)	550 (530)	270 (260)
Oklahoma City	560 (210)	180 (57)	22 (11)		870 (610)	520 (200)	190 (66)	1070 (950)	260 (470)	370 (700)		
Philadelphia (2000)	1150 (990)	390 (330)	53 (32)		330 (200)	990 (760)	190 (130)	730 (660)	130 (72)	210 (120)	230 (140)	100 (58)
Philadelphia (2004)	1310 (840)	500 (370)	110 (81)	230 (140)	270 (94)	820 (390)	230 (120)	470 (220)	68 (43)	83 (57)	130 (110)	76 (53)
Phoenix	260 (190)	68 (49)	15 (8)	65 (39)	270 (270)	330 (150)	77 (32)	160 (96)	13 (7)	16 (12)	23 (19)	15 (10)
Pittsburgh	400 (200)	81 (41)	18 (6)	33 (11)	1410 (910)	450 (150)	96 (37)	260 (140)	23 (14)	28 (20)	46 (32)	28 (21)
Providence	390 (280)	98 (63)	21 (12)	61 (30)	2590 (1610)	520 (270)	120 (51)	300 (220)	28 (23)	32 (29)	54 (49)	15 (14)
Richmond	390 (300)	100 (73)	22 (11)	96 (60)	740 (360)	390 (300)	110 (63)	190 (160)	30 (26)	26 (25)	34 (31)	29 (30)
Saint Louis	430 (170)	110 (55)	23 (9)	100 (57)	1250 (1060)	430 (110)	120 (28)	370 (110)	34 (16)	39 (13)	76 (32)	33 (12)
Salt Lake City (1999)	1060 (890)	310 (270)	470 (420)	1360 (1070)	340 (240)	1170 (1110)	130 (99)	190 (150)				
Salt Lake City (2004)	1110 (720)	220 (150)	59 (22)	120 (49)	400 (430)	930 (600)	290 (180)	890 (700)	97 (80)	110 (90)	120 (100)	94 (61)
San Diego	1570 (950)	390 (240)	580 (700)	1550 (760)	250 (140)	680 (430)	120 (75)	200 (130)	160 (140)	91 (82)		
Washington, D.C.	930 (830)	250 (220)	38 (31)	140 (110)	1630 (1290)	910 (680)	190 (130)	420 (420)	53 (54)	51 (58)	86 (100)	45 (53)

Standard deviations are given in parentheses.

[a]Not measured in 1999.

[b]Not measured in 2000.

[c]Not measured in San Diego.

different years the mean was calculated individually for each year. Carbon monoxide, a marker for combustion, had mean urban mixing ratios ranging from 150 ± 22 to 640 ± 270 parts per billion by volume (ppbv). The three highest mean values were from cities in California (San Diego, Los Angeles and Fresno, in descending order).

Methane is an important greenhouse gas that is long-lived relative to NMHCs and CO, and it is present at significantly higher background mixing ratios. Anthropogenic sources of CH_4 include energy sources (i.e. natural gas), waste treatment and landfills (Ehhalt and Prather, 2001). In the present study, mean CH_4 mixing ratios in United States cities were between 1.76 ± 0.01 and 2.25 ± 0.32 parts per million by volume (ppmv). The highest mean CH_4 mixing ratio was measured in Fresno, located in California's San Joaquin Valley. The presence of numerous feedlots and dairy operations in the region is believed to have contributed to this enhancement (Lodman et al., 1993). Background CH_4 measurements collected in September of each year at remote locations along the Western (Pacific) coast of the United States are given in Table 3, along with that year's mean urban CH_4 mixing ratio from this study (Blake, 2005; Simpson et al., 2006). Mean CH_4 levels in 20 cities showed enhancements over background levels, providing evidence for the contributions of cities in the United States to CH_4 emissions.

In the majority of the cities ethane is the most abundant NMHC, with mixing ratios between 560 ± 71 and 8740 ± 2960 pptv. While alkanes were generally the most abundant class of NMHCs, their relatively slow reaction rate with OH often makes their contribution to urban ozone production less significant than the faster reacting unsaturated species.

The most abundant unsaturated species varied between the different cities, with isoprene being the most abundant in nearly half of the cities. Biogenic emissions are the major known source of isoprene (Khalil and Rasmussen, 1992; Jobson et al., 1994), and the summertime sampling period lends itself to high mixing ratios of isoprene in cities with more vegetation. In those cities with significant biogenic emissions and relatively low vehicular emissions, the relatively fast reaction rates of isoprene and other biogenic species can make their contribution to ozone formation substantially greater than in other cities with large transportation sources. In this study, cities with the highest isoprene levels, such as Providence and Charleston, are in more densely vegetated regions, while Las Vegas and El Paso, which have the lowest isoprene values, are located in the desert. It is important to note that many of the samples were collected in locations where isoprene sources are expected to be present (i.e. parks). While care was taken to be in open areas that were removed from dense vegetation, this was not always possible and samples may represent a bias towards higher relative isoprene. In the remaining cities the most abundant species was either toluene, ethene or ethyne, all of which are transportation related, although toluene can have large non-vehicular sources. Those cities with the highest levels of toluene (Baltimore, Chicago and Los Angeles) are all large cities, and the enhancement in toluene indicates a strong industrial presence. It is also useful to note that the highly reactive benzene, toluene, ethylbenzene and xylenes (BTEX) compounds represent a significant fraction of reported unsaturated hydrocarbon species and were present at a combined mixing ratio between 1 and 4 ppbv. While not the most abundant species, their fast reaction rates with OH make their contribution to ozone formation very significant.

The highest average mixing ratios of most NMHC species were measured in Los Angeles. As the second most populated city in the United States and one of the urban areas with the most frequent annual violations of the federal ozone standard (SCAQMD, 2003), this is an unsurprising result. However, there are some notably high mixing ratios of certain NMHCs in other cities. Charleston and Pittsburgh had the two highest mean values of ethane and also had high mean values (although not the highest) of propane and the butanes. Fossil fuels

Table 3
Mean background and urban methane mixing ratios (ppmv)

Year	Background CH_4 (ppmv)	Urban CH_4 (ppmv)
1999	1.83 (0.01)	1.83 (0.07)
2000	1.81 (0.01)	1.87 (0.09)
2001	1.82 (0.01)	1.90 (0.05)
2002	1.83 (0.02)	1.98 (0.19)
2003	1.86 (0.01)	1.89 (0.07)
2004	1.84 (0.01)	1.90 (0.07)
2005	1.84 (0.01)	1.95 (0.09)

The background mixing ratios are Pacific basin data collected between 30 and 45°N. Standard deviations are given in parentheses. The 2005 urban value is Los Angeles only.

are known to outgas significant amounts of light (C_2–C_4) alkanes (EPA, 2000), and in the cases of Charleston and Pittsburgh, local coal mining and natural gas operations are thought to be the primary source of ethane and propane. A previous study in the Midwestern United States showed fossil fuel emissions from natural gas production and oil drilling and storage to have a significant impact on mixing ratios of light alkanes in Oklahoma City and, consequently, a significant impact on ozone formation (Katzenstein et al., 2003). In cities where elevated emissions of light alkanes are not coupled with increased emissions of unsaturated species (i.e. vehicular emissions), the contribution of alkanes to ozone formation can be substantial. The mean mixing ratios of C_2–C_4 alkanes reported here for Oklahoma City and also for El Paso (located on the edge of the oil producing region) are high compared to other cities and to other species. In El Paso these elevated levels of light alkanes might also be attributed to emissions from the nearby Mexican city of Juarez, however, back trajectories show transport from the oil field region with Juarez being downwind of El Paso for the sampling period (2 and 3 September 2003) (Draxler and Rolph, 2003). Additionally, these elevated alkanes are not accompanied by correspondingly elevated combustion products anticipated from Juarez, and ethane is enhanced relative to propane in El Paso, while the opposite would be expected of transport from Juarez where LPG is the primary household fuel (Blake and Rowland, 1995).

For the cities studied twice combustion products (ethene and ethyne) were enhanced relative to the alkanes in the 1st of study than in the second. Fig. 1 depicts the percent composition by species type for these cities in each year. The contribution of alkanes to total NMHC is greater in the 2nd year of study when all samples were collected away from roadsides, while the contribution of saturated species is greater in the 1st year when samples were collected at a combination of roadsides and open spaces, highlighting the increased influence of vehicular sources. The influence of location is also indicated by the change in the order of abundant species in Salt Lake City. During 1999, when samples were collected at roadsides, the most abundant species (ethyne, *i*-pentane and toluene) had transportation sources, while in 2004 the most abundant species were ethane, propane and *n*-butane (non-transportation related).

The difference in study design makes it difficult, if not impossible, to conclusively determine any trends for a particular city's ambient mixing ratios between

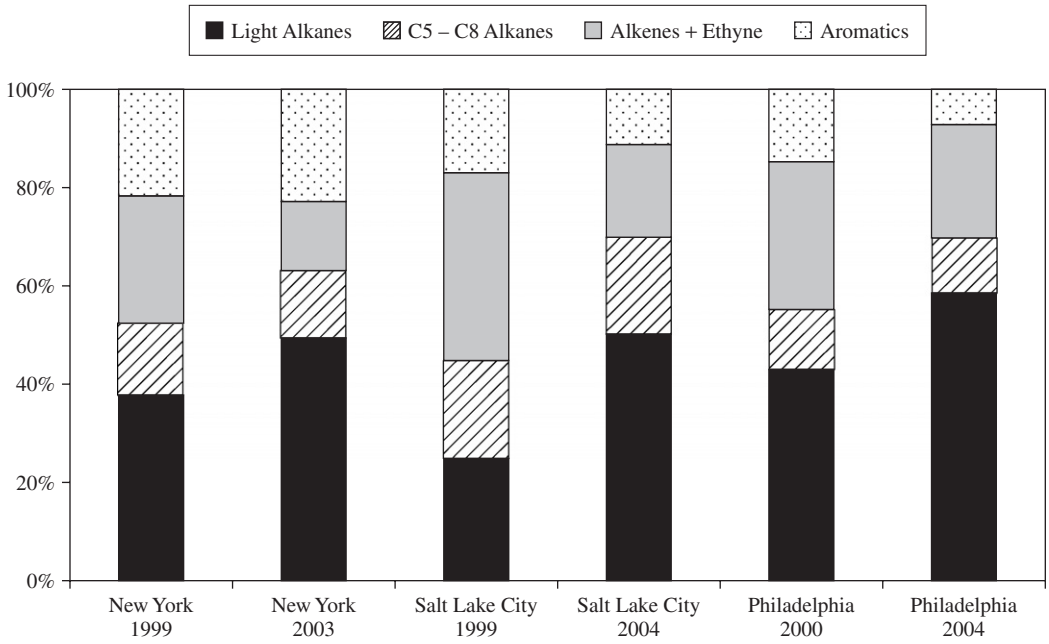

Fig. 1. Percentage contribution to total NMHC for New York, Salt Lake City and Philadelphia in both years studied. Light alkanes refers to ethane, propane, *n*-butane and *i*-butane, C_5–C_8 alkanes to *n*-pentane, *i*-pentane, hexane and octane, alkenes + ethyne to ethene, propene, 1-butene and ethyne and aromatics to benzene, toluene, ethylbenzene and *o*-xylene. For clarity, standard deviations are not shown.

Table 4
NMHC to CO ratios for individual cities (pptv [ppbv CO]$^{-1}$)

City	Ethane	Propane	*n*-Butane	*i*-Butane	*n*-Pentane	*i*-Pentane	*n*-Hexane	*n*-Heptane[a]	*n*-Octane
Baltimore	4.4 (0.57)	2.6 (0.30)	1.0 (0.37)	0.6 (0.70)	0.6 (0.60)	1.4 (0.65)	0.4 (0.60)	0.1 (0.36)	NC
Baton Rouge	NC	NC	NC	NC	NC	NC	NC	NC	NC
Birmingham	2.1 (0.72)	1.9 (0.65)	1.3 (0.89)	0.6 (0.86)	1.0 (0.82)	2.8 (0.84)	0.9 (0.72)	0.3 (0.54)	0.1 (0.71)
Boston	8.3 (0.81)	2.3 (0.30)	1.8 (0.60)	1.3 (0.32)	1.0 (0.50)	2.7 (0.44)	0.5 (0.45)	NC	0.1 (0.40)
Charleston	NC	NC	NC	NC	2.8 (0.40)	4.5 (0.48)	0.9 (0.50)	0.4 (0.45)	0.2 (0.73)
Charlotte	3.0 (0.60)	4.3 (0.77)	2.8 (0.77)	1.4 (0.88)	1.9 (0.76)	5.0 (0.90)	0.7 (0.60)	NC	0.2 (0.67)
Chicago	4.5 (0.46)	NC	1.7 (0.43)	1.2 (0.61)	1.2 (0.41)	3.3 (0.36)	0.8 (0.61)		NC
Cleveland	NC	NC	5.7 (0.79)	3.8 (0.84)	2.9 (0.80)	5.0 (0.77)	1.0 (0.82)	0.7 (0.81)	0.2 (0.73)
Denver	5.4 (0.65)	1.8 (0.31)	2.4 (0.66)	NC	1.6 (0.45)	4.4 (0.80)	0.6 (0.46)	0.2 (0.50)	0.1 (0.39)
Detroit	9.4 (0.82)	4.3 (0.52)	3.1 (0.77)	1.2 (0.45)	2.1 (0.81)	4.9 (0.80)	0.8 (0.82)	0.3 (0.76)	0.1 (0.80)
El Paso	NC	NC	NC	NC	2.3 (0.66)	6.1 (0.79)	1.2 (0.87)	0.3 (0.43)	0.1 (0.30)
Fresno	8.5 (0.95)	19.0 (0.86)	2.0 (0.68)	2.3 (0.82)	2.1 (0.90)	5.1 (0.85)	1.0 (0.96)	0.5 (0.87)	0.2 (0.97)
Houston	5.5 (0.32)	2.6 (0.43)	1.3 (0.82)	0.9 (0.69)	1.3 (0.71)	3.5 (0.79)	0.6 (0.58)		
Knoxville	4.5 (0.60)	2.6 (0.31)	4.0 (0.63)	1.2 (0.60)	2.0 (0.61)	5.7 (0.62)	0.6 (0.63)	0.3 (0.78)	1.5 (0.39)
Las Vegas	NC	NC	2.7 (0.58)	0.7 (0.64)	1.2 (0.74)	3.9 (0.71)	0.4 (0.76)	0.1 (0.88)	NC
Los Angeles	10.8 (0.80)	12.0 (0.60)	3.2 (0.32)	1.8 (0.48)	2.4 (0.61)	5.8 (0.70)	0.8 (0.65)	0.3 (0.73)	0.2 (0.84)
Milwaukee	4.6 (0.80)	5.8 (0.77)	1.0 (0.52)	0.8 (0.88)	0.7 (0.60)	1.9 (0.57)	0.7 (0.40)	NC	NC
New York City (1999)	3.6 (0.55)	2.2 (0.54)	2.4 (0.61)	1.4 (0.38)	0.9 (0.77)	3.0 (0.96)	0.6 (0.73)		NC
New York City (2003)	9.8 (0.38)	5.8 (0.53)	2.3 (0.54)	1.7 (0.67)	1.7 (0.69)	3.8 (0.64)	NC	0.6 (0.55)	NC
Oklahoma City	NC	NC	NC	NC	NC	4.7 (0.37)	NC		NC
Philadelphia (2000)	4.0 (0.96)	5.1 (0.86)	1.7 (0.65)	1.5 (0.93)	1.0 (0.73)	2.4 (0.74)	0.6 (0.88)	0.2 (0.73)	0.1 (0.61)
Philadelphia (2004)	21.2 (0.82)	10.5 (0.70)	4.6 (0.75)	4.6 (0.55)	1.5 (0.82)	3.6 (0.72)	0.7 (0.79)	0.3 (0.49)	0.2 (0.56)
Phoenix	NC	5.1 (0.60)	1.9 (0.71)	0.7 (0.71)	2.7 (0.73)	5.3 (0.84)	0.8 (0.76)	0.4 (0.60)	0.1 (0.74)
Pittsburgh	NC	NC	NC	NC	2.0 (0.42)	3.9 (0.67)	0.8 (0.58)	0.3 (0.36)	0.1 (0.61)
Providence	2.6 (0.30)	NC	2.6 (0.79)	1.8 (0.75)	1.8 (0.90)	4.9 (0.91)	0.9 (0.89)	0.5 (0.64)	0.2 (0.78)
Richmond	3.9 (0.37)	6.2 (0.84)	2.3 (0.88)	1.2 (0.78)	1.7 (0.93)	4.0 (0.93)	0.7 (0.89)	0.2 (0.87)	0.1 (0.37)
Saint Louis	7.8 (0.55)	5.1 (0.36)	3.1 (0.84)	2.7 (0.85)	1.3 (0.68)	2.6 (0.51)	0.9 (0.54)	NC	0.1 (0.49)
Salt Lake City (1999)	2.6 (0.44)	2.0 (0.78)	2.3 (0.73)	0.7 (0.73)	1.7 (0.56)	3.5 (0.61)	0.8 (0.66)		0.1 (0.54)
Salt Lake City (2004)	2.0 (0.30)	4.9 (0.50)	2.5 (0.70)	1.7 (0.61)	2.8 (0.67)	4.5 (0.72)	0.8 (0.59)	0.3 (0.46)	0.1 (0.39)
San Diego	2.6 (0.88)	3.0 (0.71)	1.0 (0.80)	0.7 (0.87)	1.0 (0.78)	2.6 (0.72)	0.4 (0.68)	0.1 (0.88)	0.1 (0.79)
Washington, D.C.	4.3 (0.71)	3.7 (0.79)	1.7 (0.91)	1.0 (0.86)	1.3 (0.93)	3.0 (0.94)	1.0 (0.86)	0.3 (0.88)	0.1 (0.86)

Table 4 (*continued*)

City	Ethene	Propene	1-Butene[c]	*i*-Butene[a,b]	Ethyne	Benzene	Toluene	Ethylbenzene	*o*-Xylene	*m*-Xylene[a]	*p*-Xylene[a]
Baltimore	2.7 (0.60)	0.7 (0.49)	0.1 (0.67)		2.2 (0.39)	0.6 (0.66)	NC	NC	NC		
Baton Rouge	NC	0.7 (0.66)	0.1 (0.65)	0.1 (0.30)	2.6 (0.60)	0.5 (0.65)	NC	0.1 (0.61)	0.2 (0.61)	0.3 (0.67)	0.2 (0.67)
Birmingham	4.3 (0.94)	1.1 (0.94)	0.2 (0.91)	0.4 (0.74)	3.7 (0.89)	1.1 (0.97)	3.1 (0.82)	0.4 (0.69)	0.4 (0.77)	0.7 (0.62)	0.4 (0.62)
Boston	4.4 (0.81)	1.1 (0.67)	0.2 (0.46)	0.7 (0.30)	2.9 (0.67)	0.9 (0.81)	2.0 (0.60)	0.2 (0.52)	0.3 (0.60)	0.4 (0.54)	0.2 (0.56)
Charleston	5.1 (0.70)	1.1 (0.70)	0.2 (0.47)	0.4 (0.47)	3.0 (0.61)	0.7 (0.70)	1.3 (0.60)	0.3 (0.61)	0.2 (0.71)	0.4 (0.75)	0.2 (0.77)
Charlotte	6.6 (0.79)	1.4 (0.76)	0.2 (0.60)	NC	4.1 (0.80)	1.1 (0.95)	3.4 (0.66)	0.5 (0.52)	0.4 (0.41)	1.0 (0.57)	0.4 (0.36)
Chicago	5.3 (0.69)	1.3 (0.68)	NC		2.9 (0.65)	0.7 (0.78)	NC	NC	NC		
Cleveland	3.9 (0.71)	0.8 (0.60)	0.2 (0.61)	0.4 (0.66)	4.8 (0.74)	1.3 (0.90)	3.0 (0.61)	0.5 (0.75)	0.5 (0.70)	0.8 (0.52)	0.6 (0.69)
Denver	4.3 (0.91)	1.1 (0.88)	0.1 (0.44)	0.3 (0.43)	4.4 (0.88)	0.9 (0.84)	1.9 (0.47)	0.5 (0.76)	0.4 (0.84)	0.7 (0.75)	0.2 (0.84)
Detroit	5.6 (0.91)	1.6 (0.88)	0.2 (0.73)	0.3 (0.76)	4.4 (0.70)	1.5 (0.90)	3.7 (0.82)	0.6 (0.78)	0.7 (0.82)	1.1 (0.76)	0.6 (0.55)
El Paso	5.3 (0.88)	1.4 (0.82)	0.3 (0.66)	0.3 (0.54)	5.4 (0.92)	1.5 (0.86)	4.0 (0.74)	0.6 (0.78)	0.7 (0.86)	1.0 (0.81)	0.6 (0.81)
Fresno	6.2 (0.95)	1.3 (0.88)	0.2 (0.91)	NC	5.8 (0.93)	0.8 (0.98)	3.4 (0.91)	0.4 (0.94)	0.5 (0.87)	0.6 (0.90)	0.5 (0.85)
Houston	7.9 (0.91)	1.5 (0.90)	0.1 (0.85)		2.7 (0.74)	0.8 (0.88)	2.9 (0.60)	1.1 (0.58)	NC		
Knoxville	6.9 (0.76)	1.7 (0.64)	0.1 (0.71)	0.3 (0.60)	4.2 (0.79)	1.0 (0.84)	1.5 (0.65)	0.5 (0.63)	0.5 (0.60)	0.7 (0.53)	0.4 (0.60)
Las Vegas	2.7 (0.76)	0.7 (0.75)	0.1 (0.60)		2.7 (0.68)	0.6 (0.81)	1.1 (0.56)	NC	NC	NC	NC
Los Angeles	5.7 (0.94)	0.8 (0.46)	0.1 (0.53)	0.5 (0.74)	6.1 (0.89)	1.0 (0.95)	3.0 (0.94)	0.6 (0.88)	0.5 (0.86)	1.2 (0.96)	0.2 (0.71)
Milwaukee	4.1 (0.86)	0.9 (0.63)	0.1 (0.59)	0.2 (0.33)	3.0 (0.71)	0.9 (0.86)	NC	0.2 (0.65)	0.2 (0.66)	0.4 (0.45)	0.2 (0.45)
New York City (1999)	4.3 (0.93)	1.1 (0.80)	0.1 (0.36)		4.1 (0.85)	0.6 (0.85)	NC	NC	NC		
New York City (2003)	5.3 (0.80)	1.1 (0.71)	0.2 (0.72)	0.5 (0.65)	3.7 (0.61)	1.0 (0.82)	4.2 (0.71)	NC	NC	NC	NC
Oklahoma City	2.3 (0.75)	0.7 (0.75)	0.1 (0.43)		2.4 (0.77)	0.8 (0.78)	NC	NC	NC		
Philadelphia (2000)	4.8 (0.96)	1.5 (0.93)	0.2 (0.93)		3.7 (0.96)	0.6 (0.95)	3.3 (0.72)	0.3 (0.64)	0.5 (0.63)	0.6 (0.71)	
Philadelphia (2004)	7.9 (0.89)	3.2 (0.75)	0.6 (0.50)	1.3 (0.89)	3.6 (0.90)	1.1 (0.88)	1.8 (0.67)	0.4 (0.76)	0.5 (0.73)	0.9 (0.63)	0.4 (0.62)
Phoenix	4.0 (0.61)	1.0 (0.62)	0.2 (0.63)	NC	3.3 (0.66)	0.8 (0.87)	2.0 (0.60)	0.1 (0.46)	0.2 (0.53)	0.4 (0.50)	0.2 (0.60)
Pittsburgh	3.3 (0.57)	0.7 (0.58)	0.1 (0.55)	NC	2.8 (0.75)	0.6 (0.62)	2.0 (0.46)	0.3 (0.65)	0.3 (0.46)	0.5 (0.56)	0.3 (0.46)
Providence	5.2 (0.94)	1.1 (0.88)	0.2 (0.75)	NC	4.7 (0.87)	0.9 (0.90)	3.4 (0.66)	0.4 (0.69)	0.5 (0.69)	0.7 (0.61)	0.2 (0.60)
Richmond	6.8 (0.96)	1.6 (0.87)	0.2 (0.69)	0.7 (0.67)	5.0 (0.98)	1.1 (0.57)	3.4 (0.80)	0.5 (0.71)	0.5 (0.76)	0.6 (0.80)	0.6 (0.76)
Saint Louis	3.5 (0.52)	1.2 (0.40)	0.2 (0.65)	1.0 (0.62)	2.9 (0.65)	0.7 ((0.67)	2.5 (0.61)	0.4 (0.55)	0.3 (0.40)	0.6 (0.60)	0.3 (0.35)
Salt Lake City (1999)	4.0 (0.83)	1.1 (0.64)	NC		3.7 (0.96)	1.0 (0.88)	3.8 (0.73)	0.4 (0.74)	0.6 (0.67)		
Salt Lake City (2004)	5.1 (0.96)	1.1 (0.90)	0.2 (0.76)	0.2 (0.45)	4.6 (0.74)	1.1 (0.87)	4.2 (0.66)	0.5 (0.68)	0.6 (0.73)	0.9 (0.85)	0.4 (0.61)
San Diego	3.5 (0.94)	0.8 (0.77)				2.8 (0.94)	0.5 (0.98)	1.6 (0.95)	0.3 (0.93)	0.5 (0.89)	0.5 (0.80)
Washington, D.C.	5.4 (0.98)	1.4 (0.93)	0.2 (0.95)	0.7 (0.86)	4.3 (0.93)	0.8 (0.99)	2.7 (0.92)	0.3 (0.92)	0.4 (0.90)	0.6 (0.90)	0.3 (0.90)

Correlation coefficients (r^2) are given in parentheses. Measurements that had no correlation with CO are marked as NC.

[a]Not measured in 1999.

[b]Not measured in 2000.

[c]Not measured in San Diego.

years. Additionally, comparison of mean mixing ratios using a *t*-test shows that most of these species have no statistically significant difference between years ($t < 2.04$ for 95% confidence interval). In New York, exceptions were the decreases in CO, ethyne, *n*-pentane and *i*-pentane. In Salt Lake City and Philadelphia only certain alkanes showed statistically significant changes (all increases); these were propane and the butanes in Salt Lake City and ethane, propane and *i*-butane in Philadelphia. However, any statistically significant changes are most likely a result of the removal of roadside locations or differences between sampling locations and likely do not represent changes in emissions.

3.2. NMHC to CO ratios

Each NMHC had a large range of mixing ratios between different cities and also within individual cities. In an urban environment ambient NMHCs are assumed to be primarily from local sources, and the use of ratios, to gain a better understanding of the pollutant mix, is based on this assumption. The strong association of CO with urban emissions makes it a useful marker for anthropogenically emitted hydrocarbon species, particularly combustion products. Table 4 gives the ratio between individual NMHCs and CO for each city, which represents the slope of their correlation plot. In some cases an outlying point considered to be non-representative of predominant sources in that city was removed from the calculation of the ratio. Despite proximity to NMHC sources, we acknowledge that more reactive species have undergone some photochemical aging, and point out that these ratios represent typical ambient ratios between NMHC and CO rather than emission ratios.

For the correlation between a particular hydrocarbon and CO, values of r^2 approaching 1.0 point to a similar or co-located NMHC and CO source. Compounds having correlations with an $r^2 < 0.3$ are considered to have no statistical correlation, and therefore no ratio is given. A value of 0.30 was chosen as it marks a significance of 95% for the minimum sample size (10 samples), with increasing significance for larger sample size, thus ensuring a significance level of at least 95% for all ratios given. Methane-to-CO ratios were not calculated because ambient urban levels of CH_4 are not dominated by local sources. Isoprene was also excluded from the ratio calculations, as its sources are believed to be predominantly biogenic and therefore unrelated to, and independent of, sources of CO. This is supported by the lack of correlation between isoprene and CO in any city, although we note that for roadside samples collected in New York and Salt Lake City isoprene was correlated with CO (0.08 and 0.33 pptv isoprene/ppbv CO with r^2 of 0.73 and 0.46, respectively). In Philadelphia there was no correlation. While isoprene has been shown to be present in vehicular exhaust (e.g. Borbon et al., 2001), our data suggest that this fraction was small during the summer in the cities studied, although a vehicular source was indicated by roadside samples collected in New York and Salt Lake City.

In many of the cities the C_2–C_4 alkane mixing ratios showed either poor or no correlation with CO, as expected for compounds that are not strongly associated with the primary urban source of CO, vehicular emissions. For example, the ambient mixing ratios of the C_2–C_4 alkanes were high relative to other species and showed no correlation with CO in cities thought to be influenced by regional fossil fuel emissions (Charleston, El Paso, Oklahoma City and Pittsburgh). In contrast, C_5–C_8 alkanes, alkenes, ethyne and aromatics, which are associated with transport-related emissions, were well correlated with CO in most cities. An exception is toluene, which had little or no correlation with CO in many cities, most likely a result of large non-transportation sector emissions, such as industrial solvent use.

An interesting case for unique sources is seen in Baton Rouge where ethene, like the alkanes, was not correlated with CO, even though it is normally well correlated (Fig. 2a). However, ethene is correlated with the light alkanes, and exhibits the strongest correlations with ethane and propane (Fig. 2b). One possible explanation for this is influence from the large number of petrochemical facilities in the Baton Rouge metropolitan area. These facilities have been shown to greatly influence levels of ethene, C_2–C_4 alkanes and hexane in nearby areas (Jobson et al., 2004).

To examine the United States as a whole, ratios were taken from NMHC to CO correlation plots using all samples from the study (Table 5). In general, the correlations between NMHC and CO for the entire dataset had lower r^2 values than in individual cities, with values below 0.6 for many species. As in individual cities, C_2–C_4 alkanes exhibited the weakest correlations or were not correlated at all with CO, and the alkenes, benzene

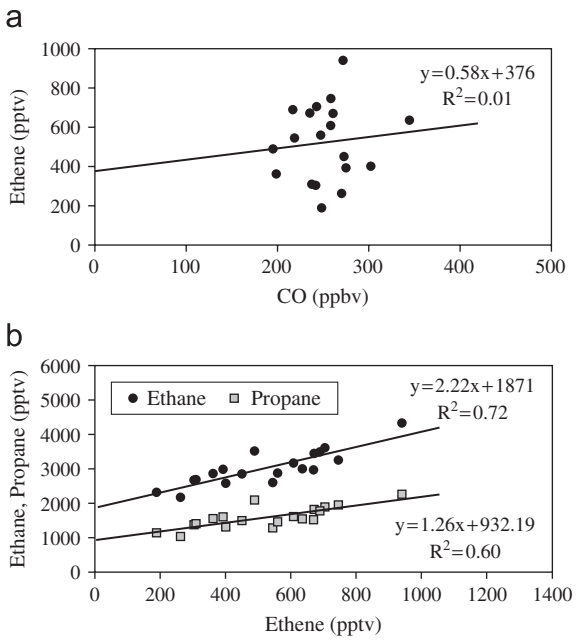

Fig. 2. Carbon monoxide (ppbv) and NMHC (pptv) mixing ratios for Baton Rouge in 2001. (a) Scatter plot of ethene vs. CO. (b) scatter plot of ethane (filled circles) and propane (shaded squares) vs. ethene.

Table 5
NMHC to CO ratios for the urban United States (pptv [ppbv CO]$^{-1}$)

Compound	All samples	
	Ratio to CO	r^2
Ethane	2.4	0.02
Propane	3.8	0.17
n-Butane	1.4	0.18
i-Butane	0.9	0.21
n-Pentane	1.2	0.44
i-Pentane	2.9	0.53
n-Hexane	0.6	0.50
n-Heptane	0.2	0.15
n-Octane	0.1	0.22
Ethene	4.1	0.74
Propene	1.0	0.63
1-Butene	0.2	0.40
i-Butene	0.3	0.36
Ethyne	3.4	0.82
Benzene	0.7	0.61
Toluene	2.7	0.44
Ethylbenzene	0.4	0.30
o-Xylene	0.5	0.40
m-Xylene	0.6	0.21
P-Xylene	0.3	0.20

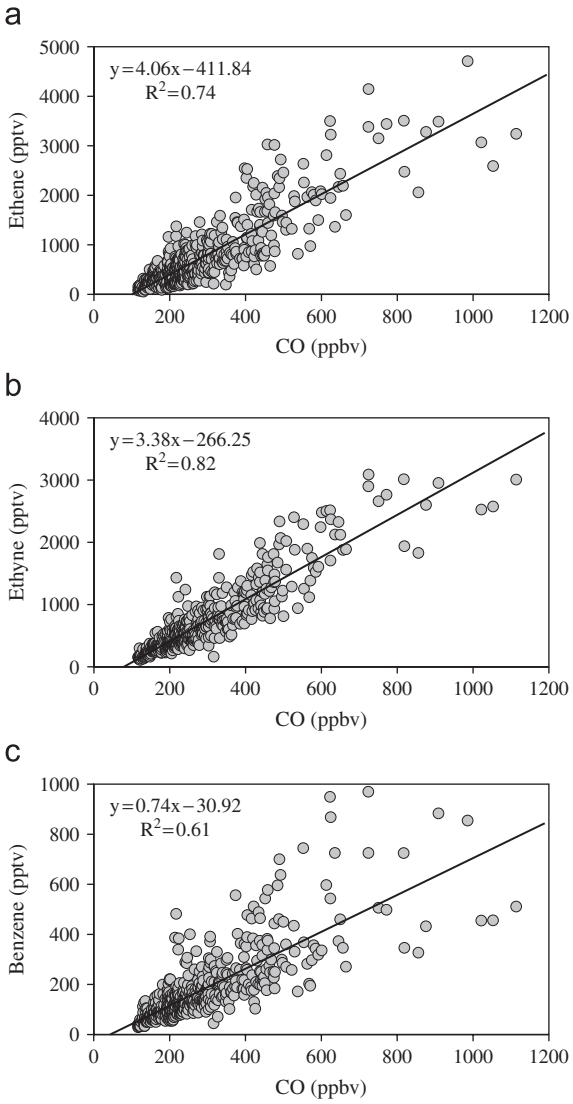

Fig. 3. Scatter plots vs. CO for all cities for (a) ethene, (b) ethyne and (c) benzene.

and ethyne had the strongest correlations (Fig. 3). *N*-pentane, *i*-pentane and *n*-hexane were correlated, although not as strongly as the combustion products. Toluene was weakly correlated with CO and ethylbenzene and the xylenes were more poorly correlated. As these data represent measurements made in 28 cities in six different years, the results show remarkable consistency within the United States. Ratios taken from the entire dataset reinforce the influence of transportation-related emissions on ambient urban mixing ratios of alkenes, C_5 and C_6 alkanes, benzene and ethyne and also point to a non-transportation source of C_2–C_4 alkanes.

4. Conclusions

Whole air canister samples were collected in 28 cities in the United States and analyzed for methane, CO and nonmethane hydrocarbons. Ethane was the most abundant NMHC in the majority of cities, and isoprene was the most abundant saturated NMHC in nearly half of the cities. To account for the variability of ambient NMHC mixing ratios, ratios of NMHCs to CO from correlation plots were analyzed. Most of the correlations had r^2 values greater than 0.6, consistent with the predominant vehicular source of CO in urban areas and indicating the significance of transportation-related NMHC sources in urban atmospheres. Unlike most other species, the C_2–C_4 alkanes had generally poor correlations with CO, indicating sources other than vehicular emissions. This was evident in those cities known or believed to be influenced by regional fossil fuel-related sources. The use of NMHC to CO ratios also allowed for the identification of unique sources of alkanes and ethene in Baton Rouge.

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